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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference PCT 1349-031/ld	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/24142	International filing date (day/month/year) 01/09/2000	Priority date (day/month/year) 07/09/1999
International Patent Classification (IPC) or national classification and IPC C09K7/02		
Applicant CROMPTON CORPORATION et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 06/04/2001	Date of completion of this report 11.12.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Krätzschmar, U Telephone No. +49 89 2399 2137 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US00/24142

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-28 as originally filed

Claims, No.:

1-30 as received on 19/11/2001 with letter of 19/11/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US00/24142

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 6-11,30
	No: Claims 1-5,12-29
Inventive step (IS)	Yes: Claims
	No: Claims 6-11,30
Industrial applicability (IA)	Yes: Claims 1-30
	No: Claims

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Ad section V.:

1. Reference is made to the following documents:

D1: US-A-4 725 372

D2: US-A-5 551 516.

2. The subject-matter of claims 1-5 and 12-29 is not considered to be novel over D1 and D2 (Art. 33(2) PCT).

D1 discloses an aqueous wellbore service fluid comprising water, a water soluble salt and a thickener in the form of a quaternary ammonium salt which may be substituted by a hydrophilic group such as hydroxyl or amide groups (see claims 1 and 4; col.1/lines 8-15; col.2/l.24 - col.3/17; col.4/17-47). The water soluble salt corresponds to the counterion of the present application and the four thickening agents mentioned in col.5, lines 60-64 seem to correspond to the structure of the gelling agent/surfactant as defined in present claims 15 and 23. The novelty of the subject-matter of present claims 15-29 is therefore anticipated by the disclosure of D1.

D2 describes similar aqueous fluid systems comprising such quaternary ammonium salts as viscoelastic surfactants. They also comprise water soluble inorganic salts (= component b) in claim 1) and stabilizing organic additives selected from organic salts and alcohols (= component c) in claim 1), see claims 3-6; col.4/l.46 - col.6/7; col.7/37-50 and col.8/52-62. D2 therefore is novelty destroying for the subject-matter of present claims 1-5 and 12-29.

3. The subject-matter of claims 6-11 and 30 does not seem to involve an inventive step according to Art. 33(3) PCT because the features of these claims are merely some out of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to provide further viscoelastic surfactant based aqueous fluid systems useful in oil field applications.

Ad section VIII.:

1. Independent claims 1, 15, 23 and 30 refer to different essential features: Whereas claim 1 pertains to an aqueous fluid comprising two additives b) and c), all the

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

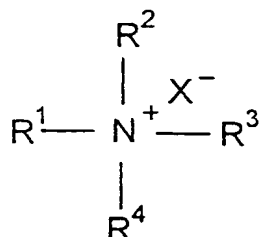
International application No. PCT/US00/24142

other claims require the presence of only one additive corresponding to compound b) in claim 1.

2. Claim 1 does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The definition of additives b) and c) in claim 1 is overlapping since both types of additives can be organic salts or organic acids.

CLAIMS:

1. An aqueous based fluid useful in oil field applications comprising:
 - a) at least one cationic surfactant having the following general structure:



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wherein R¹ is alkyl amine alkylene or alkyl amido alkylene; R² and R³ are each alkyl, hydroxy alkyl, polyalkoxy with the degree of polymerization ranging from 2 to 30, hydroxyl alkyl sulfonate, alkyl sulfonate or alkylarylsulfonate; R⁴ is hydrocarbon, saturated or unsaturated; or wherein any two of R², R³ and R⁴, together with the nitrogen atom to which they are attached, form a heterocyclic ring; and X is selected from the group consisting of halides; oxo ions of phosphorous, sulfur or chloride; and organic anions; and

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- b) at least one additive selected from the group consisting of inorganic salts, organic salts, organic acids, alcohols, and mixtures thereof.

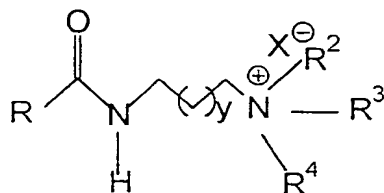
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2. The aqueous based fluid of Claim 1 wherein said fluid comprises at least one counterion selected from the group consisting of organic salts and organic acids.
3. The aqueous based fluid of Claim 1 wherein said fluid comprises at least one counterion selected from the group consisting of sulfates, sulfonates and salicylates.
4. The aqueous based fluid of Claim 2 wherein said counterion comprises at least one aromatic group.
5. The aqueous based fluid of Claim 1 wherein X is an aromatic sulfonate.
6. The aqueous based fluid of Claim 1 wherein said fluid comprises from about 0.1% to about 5% by weight of the counterion.

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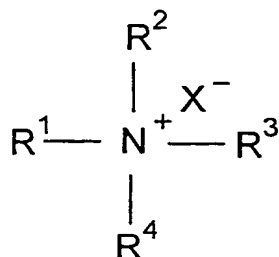
7. The aqueous based fluid of Claim 1 wherein said cationic surfactant has the following general structure:



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wherein R is saturated or unsaturated alkyl and y is an integer from 1 to 12.

8. The aqueous based fluid of Claim 7 wherein R has from about 6 to about 26 carbon atoms.
9. The aqueous based fluid of Claim 7 wherein R has from about 12 to about 22 carbon atoms.
10. The aqueous based fluid of Claim 7 wherein R is erucyl.
11. The aqueous based fluid of Claim 7 wherein y is 1.
12. The aqueous based fluid of Claim 1 wherein said cationic surfactant is isostearylamidopropylmorpholine.
13. The aqueous based fluid of Claim 1 wherein said surfactant is present in said fluid at a concentration of about 0.05% to about 10% by weight of said fluid.
14. The aqueous based fluid of Claim 1 wherein said fluid has thermal stability of greater than about 85° C.
15. The aqueous based fluid of Claim 1 in combination with a high brine liquid comprising from about 30 wt-% to about 70 wt-% salt.
16. A method of fracturing a subterranean formation comprising the steps of:
- I) providing a thickened aqueous based hydraulic fracturing fluid, comprising:
 - a) an aqueous medium; and
 - b) an effective amount of at least one gelling agent having the following general structure:



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- 10 wherein R^1 is alkylamine alkene or alkyl amidoalkene, R^2 and R^3 are each alkyl, hydroxy alkyl, alkyl, hydroxy alkyl, polyalkoxy with the degree of polymerization ranging from 2 to 30, hydroxyl alkyl sulfonate, alkyl sulfonate or alkylarylsulfonate; R^4 is hydrocarbon, saturated or unsaturated; or wherein any two of R^2 , R^3 and R^4 , together with the nitrogen atom to which they are attached,
- 15 form a heterocyclic ring; and X is selected from the group consisting of halides; oxo ions of phosphorous, sulfur or chloride; and organic anions; and
- c) at least one counterion selected from the group consisting of organic salts, inorganic salts, organic acids, alcohols, and mixtures thereof; and
- 20 II. pumping the aqueous fracturing fluid through a wellbore and into a subterranean formation at a pressure sufficient to fracture the formation.
17. The method of Claim 16 wherein said fracturing fluid comprises at least one counterion selected from the group consisting of organic acids and organic salts.
18. The method of Claim 16 wherein said counter ion is selected from the group consisting of sulfates, sulfonates and salicylates.
- 25 19. The method of Claim 17 wherein said counterion comprises at least one aromatic group.
20. The method of Claim 17 wherein said counterion is an aromatic sulfonate.
21. The method of Claim 16 wherein said gel has a thermal stability up to
- 30 temperatures of about 110° C.
22. The method of Claim 16 wherein said fracturing fluid has thermal stability of

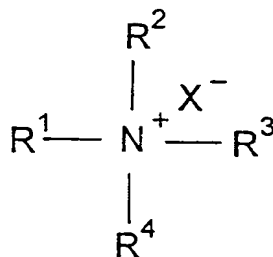
greater than about 90° C.

23. The method of Claim 16 wherein said fracturing fluid comprises from about 0.05% to about 10% by weight of said cationic surfactant.

24. A method of suspending particles in a thickened aqueous liquid the method comprising the steps of:

I) providing an aqueous medium; and

II) adding to said aqueous medium, an effective amount of at least one surfactant and at least one counterion selected from the group consisting of organic salts, inorganic salts, organic acids, alcohols, and mixtures thereof, sufficient to increase the viscosity of said aqueous medium wherein said surfactant has the following having the following general structure:



wherein R^1 is alkylamine alkene or alkyl amidoalkene, R^2 and R^3 are each alkyl, hydroxy alkyl, alkyl, hydroxy alkyl, polyalkoxy with the degree of polymerization ranging from 2 to 30, hydroxyl alkyl sulfonate, alkyl sulfonate or alkylarylsulfonate; R^4 is hydrocarbon, saturated or unsaturated; or wherein any two of R^2 , R^3 and R^4 , together with the nitrogen atom to which they are attached, form a heterocyclic ring; and X is selected from the group consisting of halides; oxo ions of phosphorous, sulfur or chloride; and organic anions.

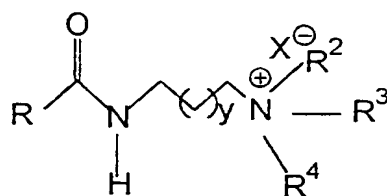
wherein said aqueous liquid is sufficiently thickened to suspend solid particulate matter.

25. The method of Claim 24 further comprising transporting the suspension of said solid particulate matter in said aqueous liquid to a remote location.

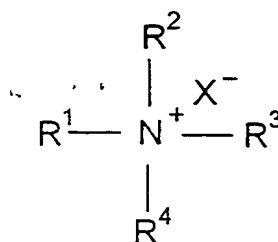
26. The method of Claim 24 wherein said solid particulate matter is selected from the group consisting of cuttings and proppants.

27. The method of Claim 24 wherein said method is implemented in a well drilling operation.
28. The method of Claim 24 wherein said method is implemented in a coil-tubing operation.
- 5 29. The method of Claim 24 wherein said method is implemented in a construction operation.
30. The method of Claim 24 wherein said method is implemented in a mining operations.
31. A method of reducing the friction exhibited by an aqueous liquid during flow
10 through a conduit comprising the steps of:
- providing an aqueous medium;
 - contacting said aqueous medium with a friction reducing amount of a viscoelastic surfactant having the following general structure:

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- 20 wherein R is saturated or unsaturated alkyl and y is an integer from 1 to 12, and an additive selected from the group consisting of inorganic salts, organic salts, organic acids, alcohols, and mixtures thereof; and
- passing said aqueous fluid through said conduit;
- 25 wherein said viscoelastic surfactant and said additive are present in an amount capable of reducing the friction exhibited by said aqueous liquid as said aqueous liquid passes through said conduit.
32. An oil field high brine completion fluid comprising:
- about 30 wt-% to about 70 wt-% of at least one inorganic or organic salt; and
 - 30 about 0.1 wt-% to about 4 wt-% of at least one cationic surfactant having the following general structure:



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wherein R^1 is alkyl amine alkylene or alkyl amido alkylene; R^2 and R^3 are each alkyl, hydroxy alkyl, polyalkoxy with the degree of polymerization ranging from 2 to 30, hydroxyl alkyl sulfonate, alkyl sulfonate or alkylarylsulfonate; R^4 is

10 hydrocarbon, saturated or unsaturated; or wherein any two of R^2 , R^3 and R^4 , together with the nitrogen atom to which they are attached, form a heterocyclic ring; and X is selected from the group consisting of halides; oxo ions of phosphorous, sulfur or chloride; and organic anions.

15 33. The fluid of Claim 32 further comprising at least one additive selected from the group consisting of inorganic salts, organic salts, organic acids, alcohols, and mixtures thereof.

20 34. The fluid of Claim 32 wherein the viscosity of said fluid increases when the temperature is increased and decreases when the temperature is decreased.